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ORDERED ORGANIC SYSTEMS AND MOLECULAR
RECTIFIERS

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I. RESEARCH PROGRAM AND PLANS

The major effort of this research program is the fabrication and study of organic and organo-metallic molecular arrays in thin film form. The films are prepared by the Langmuir-Blodgett technique, which permits the deposition of one or two monolayers at a time. Specifically, we have developed the necessary techniques to deposit layers of fatty acids and their salts by this method and are engaged in the determination of their structural and magnetic parameters. The intent of these studies is to enable us to construct two-dimensional arrays whose structures are completely characterized, and to use this knowledge in fabricating two-dimensional magnetic arrays to test various models of magnetic ordering. In addition an ambitious synthetic organic program is underway with the aim of synthesizing a molecule with asymmetric electron tunneling characteristics. It is planned to create monolayers of such "molecular rectifiers" using the Langmuir-Blodgett technique and to study their electrical characteristics. Such arrays can be considered the ultimate in microminaturization of electronic components

ACCOMPLISHMENTS

II. A. X-RAY DIFFRACTION FROM ORGANIC FILMS OF FEW MOLECULAR THICKNESSES.

We are using the well-known Langmuir-Blodgett technique to produce monomolecular layers of organic materials deposited on solid substrates. In order to characterize these films we have examined them by X-ray diffraction. The materials used are long-chain fatty acids; stearic acid, $C_{18}H_{36}O_2$, combined with Mn^{+2} is typical. The length of each molecule is about 25Å, and since the Langmuir-Blodgett technique usually produces a bi-molecular unit cell, the lattice spacing is about 50Å. With ordinary X-radiation of wavelength $\lambda=1.5\text{\AA}$ (Cu K α), the first Bragg diffraction peak is at an angle of incidence to the plane of the film of about 1° . To study diffraction so near the direction of the incident beam requires excellent collimation and spectral purity. Fortunately, such an X-ray diffractometer is available at IBM and has been used to make new and interesting observations on the structure of monolayer films.

In particular, we have observed that for small numbers of layers (we have studied odd numbers of layers to 11), in addition to the usual Bragg reflections there are subsidiary maxima whose number and intensity depend on the number of layers and the order of the reflections. This general result is well known in the physical optics of diffraction gratings with a small number of slits. Our X-ray results differ significantly from the optical case in that the intensity of the subsidiary maxima can be stronger than the principal maxima for angles below the first order Bragg peak. In addition, for all angles the relative intensities of the subsidiary to principal are larger than in the optical case. Also, the number of subsidiary peaks differs from that in the simple optical grating.

Using a computer program developed by A. Segmuller of this laboratory, who is collaborating in this work, we have calculated the diffraction from a model structure composed of layers of various refractive indices.

It is possible to reproduce the general behavior observed in the experiments. Moreover we believe the calculations can be used to obtain a rather refined structural analysis of the films. Since the films are composed of stearate anions bonded to divalent metal cations, it is reasonable to assume that the structure of the stearate ion is similar to that observed in other lattices, e.g., in crystalline stearic acid. Thus, the principal unknown part of the structure is the position of the metal cations. By calculating the diffraction with various metal positions, the best location to account for our observations can be found. Such analysis requires knowledge of the density of the films which we are attempting to establish accurately. Regardless of the refined structure that may be determined, the fact that we get good agreement between calculated and observed diffraction implies that the films correspond well to the model; i.e., they are flat and of the correct average number of layers.

B. MAGNETIC TRANSITIONS IN MULTILAYERS OF MANGANESE STEARATE.

As outlined in the contract proposal (Section III), the nature of phase transitions in systems of dimensionality less than three is a problem of great interest. The Langmuir-Blodgett technique allows one to produce monomolecular layers whose lattice spacing between ionic ends of molecules is about 50Å. If magnetic ions were attached to these molecular units they would be essentially magnetically isolated in planes, i.e., in two dimensions. In the Langmuir-Blodgett technique there would, in fact be two magnetic ions in the third dimension; so that it is nearly two dimensional. One might avoid even this approximation by making a single layer, in which the magnetic atoms are held in place by the long hydrocarbon chain which itself has no magnetic effect. We have been attempting to achieve this using the manganese salt of stearic acid.

Briefly, our result thus far is that we have produced films of manganese stearate (abbr., MnSt₂) by the Langmuir-Blodgett technique. We find that they can be prepared in multilayers. In our largest sample, 500 layers were deposited.

We have searched for magnetic effects in the film samples using electron spin resonance (ESR) because of its high sensitivity and simplicity. We found that in the 500 layer sample a magnetic transition occurred, as evidenced by a dramatic broadening and shifting of the ESR line at temperatures below about 4°K. These effects could arise from the development of a spontaneous internal magnetization in the sample.

We also prepared large quantities of crystalline MnSt₂ powder and studied this compound by other means. We verified that the MnSt₂ powder also undergoes a magnetic transition similar to that of the films. In addition, the powder was studied in a magnetic force balance from which its magnetic moment and susceptibility as functions of temperature and field were measured. The result was that at about 4°K the powder develops a small spontaneous magnetization. From the small size of the

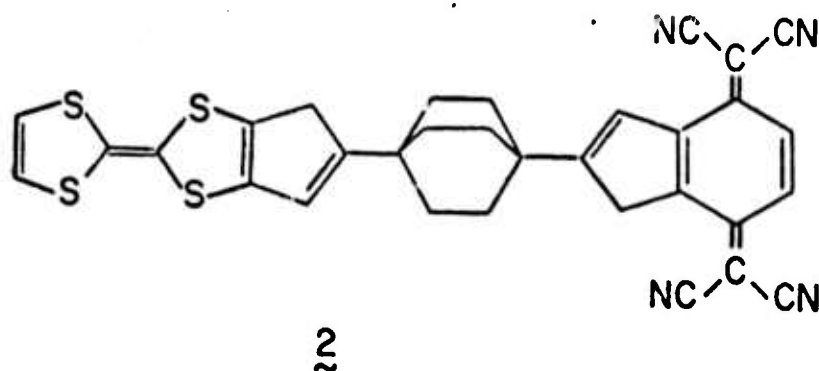
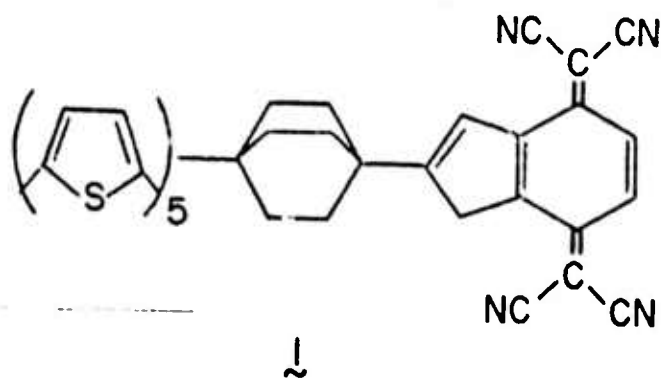
3.

magnetization and the spin resonance results, we tentatively hypothesize that MnSt_2 , in multilayers and in crystalline powder, undergoes a transition to a so-called "weak ferromagnetic" state at $T=4^\circ\text{K}$.

C. MOLECULAR RECTIFIER SYNTHESIS

This program involves the synthesis of a simple electronic rectification device based on a single organic molecule. Such a molecular rectifier consists of a donor π system and an acceptor π system, separated by a sigma-bonded (methylene) tunneling bridge. We have calculated the response of such a molecule to an applied electric field, and have found that current will flow only from left to right in the sandwich system: cathode-acceptor- σ bridge-donor-anode (Chem. Phys. Lett. 29 (2), 277, 1974).

Such an array can in principle be constructed using the Langmuir-Blodgett technique to deposit the rectifier molecule on a metal film, followed by evaporation of the second electrode. The molecules chosen for synthesis as rectifiers are compounds 1 and 2 below. They consist of low ionization potential organosulfur donors connected through a rigid bicyclo-octane bridge to a tetracyanoquinodimethane (TCNQ) acceptor. Since the donor and acceptor parts of the complete molecules would react with each other (charge transfer) if allowed to come directly in contact as separate entities, the synthesis of the rectifier molecules must proceed through many carefully planned steps to prohibit such reaction. The entire planned sequence of reactions is shown in the Appendix. At the present time we have completed steps 1 through 9, as well as 12 and 13, in the synthesis of molecule 1.



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III. PROBLEMS ENCOUNTERED AND PROGRAM CHANGES

None

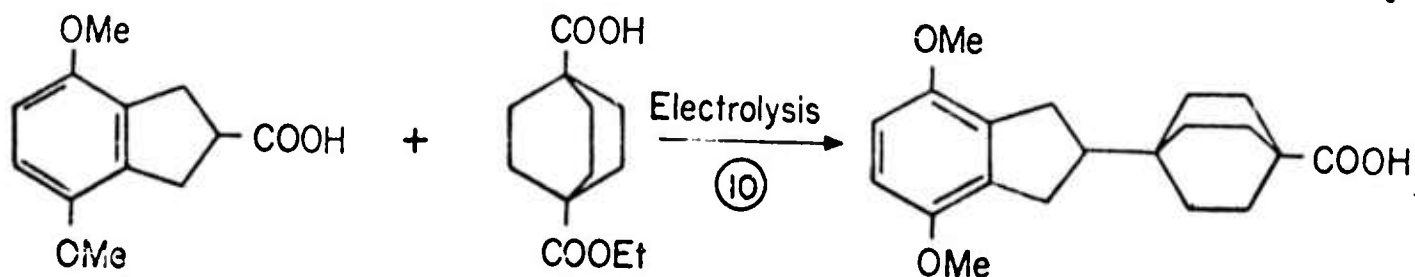
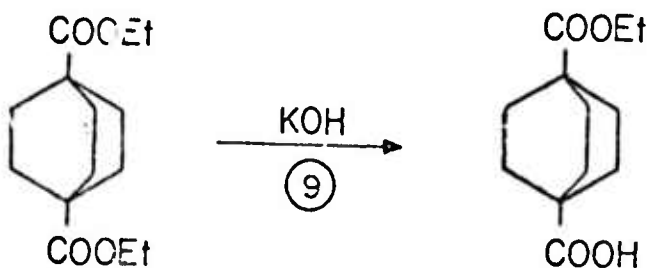
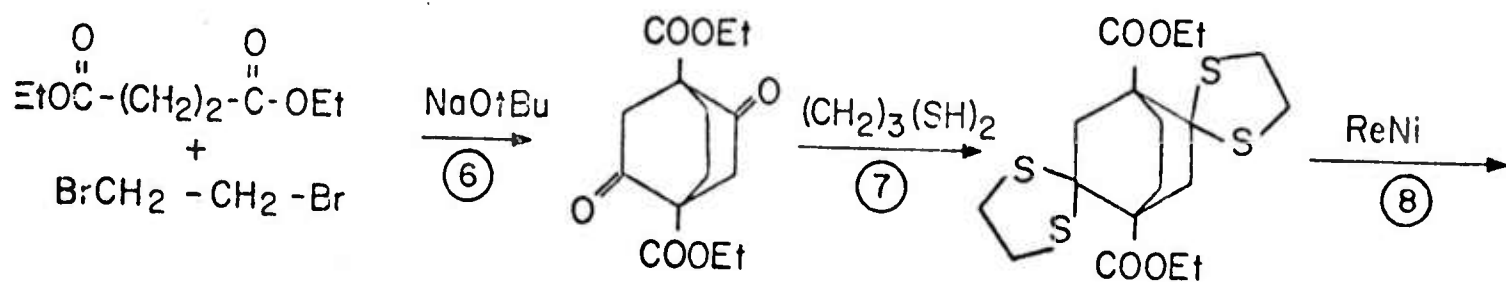
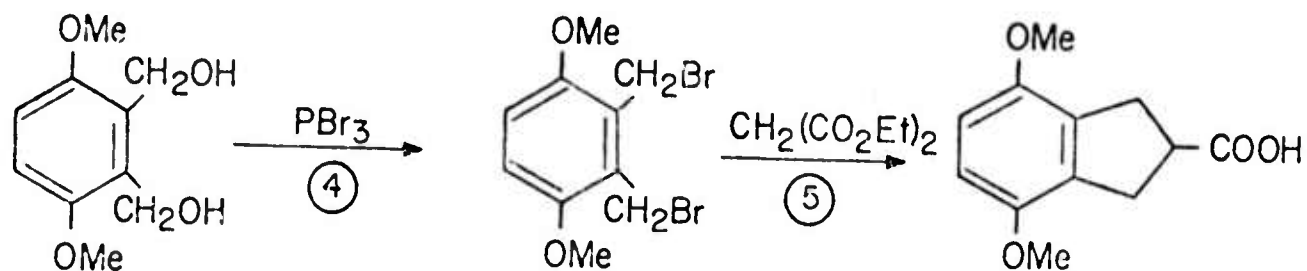
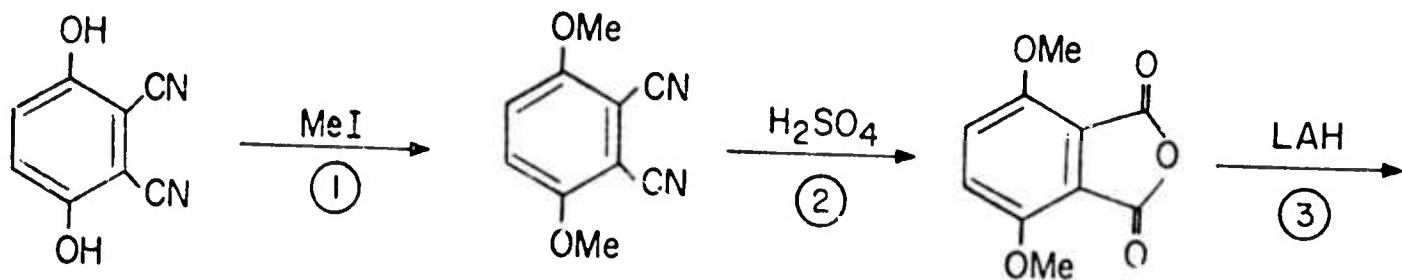
IV. FISCAL STATUS

Expenditure and commitments to date are on schedule with the contract.

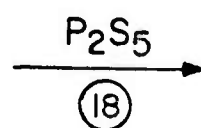
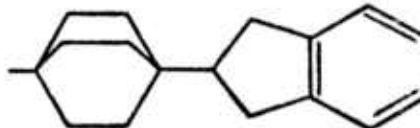
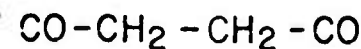
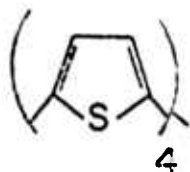
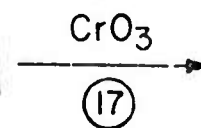
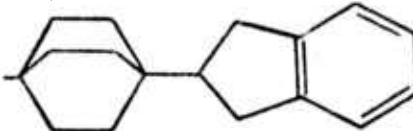
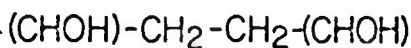
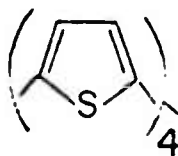
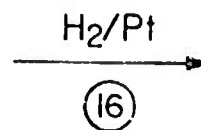
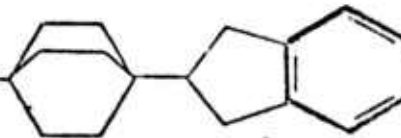
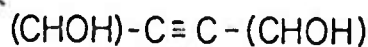
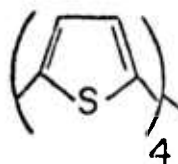
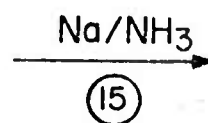
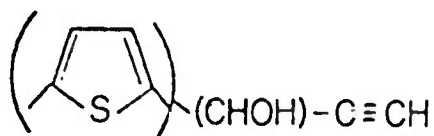
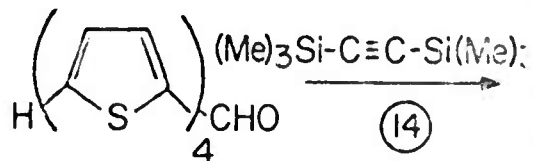
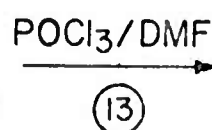
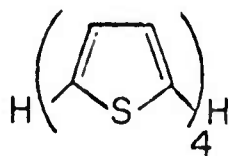
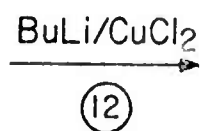
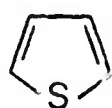
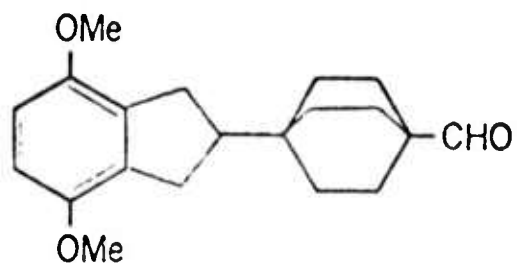
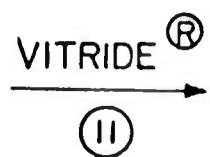
V. FUTURE PLANS

We are currently working to improve the sensitivity of the ESR spectrometer so that we can observe single monolayers of MnSt_2 , in order to test whether the magnetic transition persists in a truly two-dimensional structure. We are also preparing a large quantity of MnSt_2 powder with which to do neutron scattering. Neutron scattering can establish the magnetic structure in the ordered state and determine whether the MnSt_2 is a "weak ferromagnet" or a ferrimagnet. This experiment will be carried out in collaboration with workers at Brookhaven National Laboratory.

The successful steps completed toward the molecular rectifier synthesis are to be repeated to provide large quantities of material to continue the synthesis. In addition, we are engaged in determining the reaction conditions for step 10 (Appendix), which must be carried out electrochemically in a special cell designed to remove the reaction product. This step will connect the donor precursor to the insulating σ -bridge.



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